

and the alkylation of the corresponding ethers,<sup>5</sup> respectively. In each case alkylation leads to formation of oxonium ions quantitatively. No exchange between excess alkylating agents and oxonium ions 3-6 and 23-25 was observed on the nmr time scale between 0 and -78°.

The alkylation of *t*-butyl mercaptan and diethyl and diisopropyl thioethers with ions 1a,b and 2a,b yields sulfonium ions 19-21 and 36-37, respectively. The pmr spectra of these sulfonium ions correlate very well with those reported previously for protonated mercaptans and thioethers.<sup>6</sup>

When aldehydes, ketones, and carboxylic acids are added to SO<sub>2</sub> solutions of ions 1a,b and 2a,b immediate and exclusive alkylation on oxygen occurs with formation of oxonium ions 7-15 and 26-33. In the cases of the alkylation reactions of unsymmetrically substituted ketones, aldehydes, and carboxylic acids the formation of at least two isomeric forms of the resulting oxonium ions is observed. Except for alkylated formic acid, the spectra of only those isomers present in highest concentration are shown in Table I.

The chemical shifts, multiplicities, and coupling constants of the pmr spectra of oxonium ions 7-15 and 26-33 are very similar to those obtained from protonation of the same aldehydes,<sup>7</sup> ketones,<sup>8</sup> and carboxylic acids.<sup>9</sup> Particularly diagnostic in the case of aldehydes is the chemical shift of the proton on the carbonyl carbon. These range from  $\delta$  9.42-9.95 for ions 11, 12, 29, and 30. For ions 11 and 29 these signals appear as 1 H quartets ( $J = 3.5$  Hz) with the corresponding 3 H methyl signals at  $\delta$  3.51 and 3.46 ( $J = 3.5$  Hz). Similarly for alkylated carboxylic acids 13-15 and 31-33 the OH protons appear between  $\delta$  12.54 and 13.06. The chemical shifts of the CH<sub>3</sub>Y methyl and CH<sub>3</sub>CH<sub>2</sub>Y ethyl groups in ions 7-15 and 26-33, respectively, are to slightly lower field than in the oxonium ions 3-6 and 23-25, as expected.

The reaction of diethylamine with ions 1a,b and 2a,b yields the corresponding tetralkylammonium ions 22 and 38, respectively. Although alkylation was obvious from the pmr spectra of ions 22 and 38, pronounced broadening of peaks characteristic of long-range coupling is observed.

Upon addition of nitro alkyl or aryl compounds to solutions of excess of ions 1a,b and 2a,b pmr spectra of the solutions obtained are consistent with the formation of ions 16-18, 34, and 35, respectively. These alkylalkoxyoxonium cations are isoelectronic with carboxylic acid esters and are important primarily because of mechanistic implications for alkylation of nitroaromatic compounds. This subject is discussed in detail in forthcoming publications.

The alkylation data presented demonstrate the general alkylating ability and synthetic utility of dialkylhalonium ions.<sup>10</sup> As opposed to alkylation with

Meerwein's oxonium salts<sup>11</sup> the synthetic advantage of alkylation with dialkylhalonium ions lies in their easy preparation and especially in their greater alkylating ability and wide range in selectivity. Many of the fluoroantimonate salts of ions 4-35 can be isolated upon evaporation of solvent, excess methyl halides, and corresponding precursor.<sup>1</sup> For example, isolation of the hexafluoroantimonate salt of ion 18 as a crystalline solid (90%, mp 90-91°) can be accomplished. This new preparative method makes available readily the entire scope of onium ion salts of both synthetic and theoretical interest.

The dialkylhalonium ion complexes were also found to effect C alkylations which will be reported in a following publication.<sup>12</sup>

**Acknowledgment.** Partial support of the work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(12) G. A. Olah, J. R. DeMember, and M. Tashiro, to be published.

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Received January 27, 1970

### Comparison of the Reactivity of Singlet and Triplet States of Cyclic Alkanones toward the $\alpha$ -Cleavage Process. An Unexpected Reactivity Difference between $n,\pi^*$ Singlet and Triplet<sup>1</sup>

Sir:

One of the more intriguing questions in organic photochemistry is whether the differences in spin multiplicity between excited singlet and triplet states will be reflected in their reactivity toward primary photochemical processes. In the case of alkyl ketones, a number of reports have recently appeared which compare the reactivity of  $n,\pi^*$  excited singlet and triplet states in solution toward such primary photochemical processes as cycloaddition to olefins<sup>2</sup> and inter-<sup>3</sup> and intramolecular<sup>4</sup> hydrogen abstractions. To date, however, there have been no reports of the relative reactivities of alkyl ketone singlet and triplet states toward the primary photochemical process of  $\alpha$  cleavage.

Yang and Feit<sup>5</sup> have provided evidence that  $\alpha$  cleavage occurs from both the singlet and triplet excited states of *t*-butyl methyl ketone and have measured the quantum yields for reaction from the two states. Knowledge of the efficiency of a process, *i.e.*, the quantum yield, is, however, not sufficient to determine the reactivity toward that process.<sup>6</sup> Also, in a number of cyclopentanone and cyclohexanone systems,<sup>7-9</sup>

(5) B. M. Ramsey and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 3058 (1966), and references therein.

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(9) G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

(10) Similar indications have recently been reported by Peterson, Clifford, and Slama in the study of alkylation with tetramethylenehalonium ions; presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstracts, ORGN 109.

(1) (a) Molecular Photochemistry. XXII. For paper XXI see N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970). (b) The authors wish to thank the Air Force Office of Scientific Research for their generous support of this work through Grant AFOSR-68-1381.

(2) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **90**, 6863 (1968); N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970).

(3) P. J. Wagner, *ibid.*, **89**, 2503 (1967).

(4) N. C. Yang and S. P. Elliott, *ibid.*, **90**, 4194 (1968).

(5) N. C. Yang and E. D. Feit, *ibid.*, **90**, 504 (1968).

(6) The reactivity of an excited state toward a primary photochemical process is a measure of the rate constant for the process. See N. J. Turro, *J. Chem. Educ.*, **44**, 536 (1967).

Table I. Photoisomerization of Cycloalkanones to Unsaturated Aldehydes

Ketone	Aldehyde <sup>a</sup>	$\Phi_A^b$	$k_q\tau_T^c$	$\tau_T$ , nsec <sup>d</sup>	$\tau_s$ , nsecs <sup>e</sup>
 1K	 1A	0.11 (0.25) <sup>f</sup>	(47) <sup>f</sup>	9.5	1.9
 2K	 2A	0.26	1.4	0.28	2.7
 3K	 3A	0.61	$\leq 0.1^g$	$\leq 0.02$	8.7
 4K	 4A	0.28	0.3	$\leq 0.02$	5.2
 5K	 5A	0.25	$\leq 0.1^g$	$\leq 0.02$	4.2
 6K	 6A	0.26	$\leq 0.1^g$	$\leq 0.02$	3.8
 7K	 7A	0.12 (0.12) <sup>h</sup>	$\leq 0.1^g$	$\leq 0.02$	4.4

<sup>a</sup> Aldehydes were characterized by their spectral properties. <sup>b</sup> Quantum yields for aldehyde formation were determined with 0.1 M degassed solutions of ketone in benzene at 3130 Å using a merry-go-round apparatus and benzophenone-benzhydrol actinometry. Photolyses were run to 10% conversion. Error limits are  $\pm 10\%$ . <sup>c</sup> Slope of Stern-Volmer plot for quenching of aldehyde formation by 1,3-pentadiene in benzene. Error limits  $\pm 20\%$ . <sup>d</sup> Cyclic alkanone excited triplet-state lifetime calculated assuming that  $k_q = 5 \times 10^9 M^{-1} \text{sec}^{-1}$  in benzene. <sup>e</sup> Cyclic alkanone excited singlet-state lifetime measured by monitoring the fluorescence decay by the single-photon counting technique in acetonitrile at 435 nm. For a discussion of this technique see J. B. Birks and I. H. Munro, *Progr. Reaction Kinetics*, **4**, 215 (1967). <sup>f</sup> From ref 9. <sup>g</sup> No quenching ( $\pm 10\%$ ) observed up to 2 M 1,3-pentadiene. <sup>h</sup> From ref 12d, measured in *n*-heptane.

quenching studies have indicated that the photo-products resulting from  $\alpha$  cleavage in solution arise solely from the  $n, \pi^*$  triplet state. Without knowledge of the rate constants for intersystem crossing in these ketones, it is impossible to make rigorous conclusions about the relative singlet- and triplet-state reactivities. That intersystem crossing was rapid enough to swamp out singlet reaction occurring with a rate constant similar to that for  $\alpha$  cleavage from the triplet state could not be ruled out.

We report results which allow for the first time a determination of the respective reactivities of  $n, \pi^*$  singlet and triplet excited states of a number of cyclic alkanones toward the  $\alpha$ -cleavage process.

A quantitative investigation of the photoinduced conversions of the mono- and bicyclic ketones **1K**–**7K** to the respective unsaturated aldehydes **1A**–**7A** in benzene solution was carried out (see Table I). Previously, aldehyde formation, as a primary photoprocess in solution, has been reported for cyclopentanone (**1K**),<sup>7,10</sup> norcamphor (**4K**),<sup>10,11</sup> and camphor

(**7K**).<sup>10–12</sup> The quantum yields for aldehyde formation and slopes derived from Stern-Volmer plots for quenching of aldehyde formation by *trans*-1,3-pentadiene are also given in Table I.

Measurable quenching was observed only for **1K** and **2K**. The triplet lifetimes ( $\tau_T$ ) of these ketones were obtained from the slopes of the Stern-Volmer plots. The small amount of quenching observed with norcamphor (**4K**) can be attributed primarily to quenching of the  $n, \pi^*$  singlet state.<sup>13</sup> Thus, within experimental error, no piperylene quenching of aldehyde formation by up to 2 M 1,3-pentadiene is observed for **3K**–**7K**.<sup>14</sup> This implies the following possibilities:  $\alpha$  cleavage of ketones **3K**–**7K** is occurring (a) solely from a rapid reaction of the  $n, \pi^*$  triplet state, (b) solely from the  $n, \pi^*$  singlet state, or (c) partially *via* a rapid triplet

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(13) F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 1793 (1970).

(14) Professor Jack Saltiel of Florida State University has informed us that his group has also observed no quenching of the photorearrangement of camphor to **7A** by up to 0.2 M 1,3-pentadiene.

(7) P. Dunion and C. N. Trumbore, *J. Amer. Chem. Soc.*, **87**, 4211 (1965).

(8) R. Simonaitis, G. W. Cowell, and J. N. Pitts, Jr., *Tetrahedron Lett.*, 3751 (1967).

(9) P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969).

and partially *via* a singlet reaction. If either (a) or (c) holds, then the absence of piperylene quenching allows estimation of the upper limits for  $\tau_T$  of **3K-7K** (Table I). On the other hand, if  $\alpha$  cleavage occurs totally from the singlet state, then clearly efficient piperylene quenching would not be expected and nothing can be safely concluded about the  $\tau_T$  values extracted from our Stern-Volmer plots.

By analogy,<sup>7,8,9</sup> we would expect the  $n,\pi^*$  triplet state of cyclic ketones **3K-7K**, if produced, to undergo  $\alpha$  cleavage and subsequent rapid disproportionation to **3A-7A**.<sup>7-9</sup> Thus, for reaction to occur solely from the  $n,\pi^*$  singlet there would have to be little or no intersystem crossing in these ketones. This could be the case if the rate constant for  $\alpha$  cleavage from the singlet,  $k_r^s$ , were much larger than the rate constant for intersystem crossing,  $k_{st}$ . But if  $k_r^s \gg k_{st}$ , then the singlet lifetimes,  $\tau_s$ , will be approximately  $1/k_r^s$  and hence determined primarily by  $k_r^s$ . However, we will show below that this possibility can be experimentally ruled out.

The introduction of either  $\alpha$ -methyl substituents<sup>9</sup> or ring strain<sup>7-9</sup> in cyclic alkanones has been shown to increase the value of  $k_r^T$ . That ring strain and  $\alpha$  substitution will similarly affect  $\alpha$  cleavage of  $n,\pi^*$  singlet states seems quite reasonable. Thus, if singlet lifetimes are determined by  $k_r^s$ , then  $\tau_s$  should decrease with increasing angle strain or  $\alpha$ -alkyl substituents.

On the contrary, ketones **3K-7K** all have  $\tau_s$  values larger than that of cyclopentanone, with **3K** being over four times greater. This implies that  $\tau_s$  for **3K-7K** is primarily determined *not* by  $k_r^s$ , but rather by  $k_{st}$ , which for alkyl ketones decreases with increasing substitution of  $\alpha$ -methyl groups.<sup>15</sup> Thus, we conclude that  $\alpha$  cleavage of the ketones **3K-7K** must arise, at least in part, from the  $n,\pi^*$  triplet state. The lack of quenching of aldehyde formation by piperylene can then safely be used to determine the upper limits for  $\tau_T$  of **3K-7K** given in Table I.

Since radiationless deactivation of alkyl ketone triplets is relatively inefficient,<sup>16</sup>  $k_r^T$  can be approximated by  $\tau_T^{-1}$ . Thus, for ketones **3K-7K**,  $k_r^T$  must be greater than  $5 \times 10^{10} \text{ sec}^{-1}$ . On the other hand,  $1/\tau_s$  must be an upper limit for  $k_r^s$ . Since the singlet lifetimes of **3K-7K** range from 4 to 9 nsec, we conclude that  $k_r^s < 2.5 \times 10^8 \text{ sec}^{-1}$ . Hence there is a difference of at least two orders of magnitude in the reactivity of the  $n,\pi^*$  singlet state and the  $n,\pi^*$  triplet state of these cyclic alkanones toward  $\alpha$  cleavage. The source of this striking reactivity difference toward  $\alpha$  cleavage for these cyclic alkanone singlets and triplets, which is of considerable interest, is being actively investigated.

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(16) P. J. Wagner, *J. Amer. Chem. Soc.*, **88**, 5672 (1966).

(17) National Institutes of Health Predoctoral Fellow, 1966-1969.

(18) National Institutes of Health Predoctoral Fellow, 1966-1969.

(19) National Institutes of Health Postdoctoral Fellow, 1968-1969.

(20) Alfred P. Sloan Fellow, 1966-1970.

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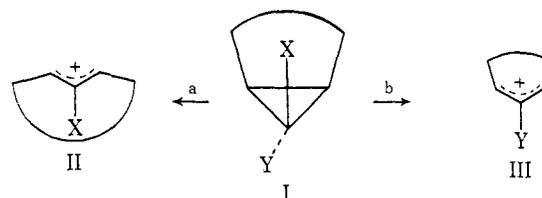
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Received September 11, 1969

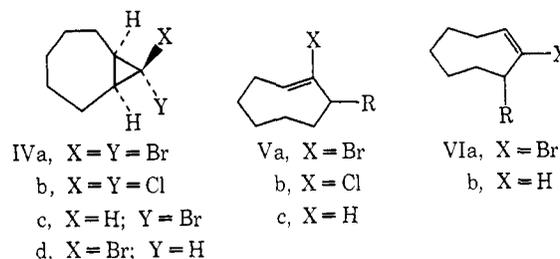
## Silver Perchlorate Promoted Ring Expansion of Halocarbene Adducts of Cyclic Olefins. A Facile Synthesis of *trans*-Cyclooctene and *trans*-Cyclononene Derivatives

Sir:

The ring expansion of halocarbene adducts of cyclic olefins is now well established as a synthetic reaction of considerable utility.<sup>1,2a</sup> Recently, the application of the principle of orbital symmetry conservation to this reaction<sup>3</sup> has led to the prediction that the ring expansion of dihalocarbene adducts (I, X = halogen; Y = halogen) should follow one of two pathways (a or b, Scheme I). It then seemed likely from steric considerations<sup>4</sup> that pathway a, involving the *exo*-leaving group (Y) and leading to a *trans,trans*-allyl cation (II) (and hence to a *trans* olefin derivative), would be preferred unless the expanded ring were too small to accommodate a *trans* double bond. In the latter case, pathway b would be preferred. Clearly, pathway b is prohibited for *exo*-monohalocarbene adducts (I, X = H; Y = halogen) and pathway a for *endo* adducts (I, X = halogen; Y = H).



In contrast to its thermal stability<sup>2a</sup> we now report that when 8,8-dibromobicyclo[5.1.0]octane (IVa) was treated with an excess of silver perchlorate in anhydrous methanol solution at 20°, it was quantitatively converted in less than 5 min into *trans*-2-bromo-3-methoxycyclooctene<sup>5</sup> (Va, R = OMe) [nmr  $\tau$  3.89 (dd,  $J = 4$  and 11.5 Hz, 1 H), 6.38 (dd, 1 H), 6.81 (s, 3 H), 7.0-9.4 (m, 10 H)]. When Va (R = OMe) was heated in a nitrogen atmosphere at 170-180° for 140 min, it underwent ca. 75% conversion to its *cis* isomer (VIa, R = OMe) [ $\tau$  3.78 (t,  $J = 8.5$  Hz, 1 H), 5.90 (t,  $J = 7.5$  Hz, 1 H), 6.80 (s, 3 H), 7.6-8.8 (m, 10 H)].



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(3) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(4) C. H. De Puy, *Accounts Chem. Res.*, **1**, 33 (1968).

(5) Satisfactory analytical and spectroscopic data were obtained for all new compounds described.

(6) Nmr spectra of  $\text{CCl}_4$  solutions were measured at 100 MHz with a Varian HA 100 spectrometer. Me<sub>4</sub>Si was used as internal standard, and chemical shifts are given in parts per million on a  $\tau$  scale.